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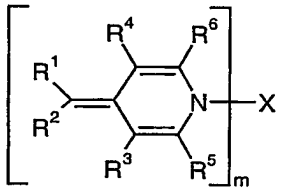
(54) Title: SUNSCREEN COMPOSITIONS AS WELL AS DIHYDROPYRIDINES AND DIHYDROPYRANES

(57) Abstract: 1,4-dihydropyridine and 1,4-dihydropyrane derivatives and novel cosmetic or dermatological sunscreen compositions containing novel and/or known 1,4- dihydropyridine or 1,4-dihydropyrane derivatives which are useful for photoprotecting human skin and/or hair against UV radiation, in particular solar radiation, and the use of such 1,4-dihydropyridine and/or 1,4-dihydropyrane derivatives as UV-A screening agents, particularly in cosmetic and pharmaceutical compositions.

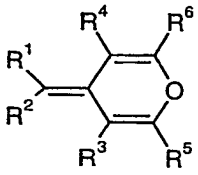
SUNSCREEN COMPOSITIONS AS WELL AS DIHYDROPYRIDINES AND DIHYDROPYRANES

The present invention relates to novel 1,4-dihydropyridine and 1,4-dihydropyrane derivatives, to novel cosmetic or dermatological sunscreen compositions containing certain novel and/or known 1,4-dihydropyridine or 1,4-dihydropyrane derivatives which are useful for photoprotecting human skin and/or hair against UV radiation, in particular solar radiation, and to the use of such 1,4-dihydropyridine and/or 1,4-dihydropyrane derivatives as UV-A screening agents, particularly in cosmetic and pharmaceutical compositions.

More particularly, in one aspect the invention relates to novel cosmetic or dermatological sunscreen compositions comprising a 1,4-dihydropyridine derivative of the general formula I or a 1,4-dihydropyrane derivative of the general formula II



(I)



(II)

wherein

m is 1 or 2;

R^1 and R^2 are identical or different electron-withdrawing groups, or one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is an electron-withdrawing group;

R^3, R^4, R^5, are R^6 are, independently, hydrogen, alkyl, cycloalkyl or aryl;

R^3 and R^5 and/or R^4, and R^6 taken together with the carbon atoms to which they are attached, may form a 5 or 6 membered ring which optionally is substituted with one to four alkyl, cycloalkyl or alkoxy groups;

X is a moiety R^7, when m is 1; and is alkylene or poly(oxyalkylene) when m is 2; and

R^7 is hydrogen, alkyl, cycloalkyl, alkoxyalkyl or aryl.

As used herein the term "electron-withdrawing groups" refers to groups containing a multiple bond such as a nitrilo (-CN) group or a -$COOR^8$, -COR^8 or –$CONR^8$ group, wherein R^8 is hydrogen, alkyl, cycloalkyl or aryl. Alkyl, alone and in combination with alkoxy refers to saturated straight or branched chain hydrocarbon groups containing 1 to 21, preferably 1 to 8 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, sec. butyl,

isobutyl, pentyl, neopentyl, hexyl, 2-ethyl-hexyl, and octyl. Alkoxy, alone and in combination with alkyl refers to alkyl groups as defined above which are bound through an oxygen.

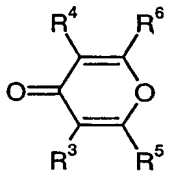
Aryl refers to aromatic, optionally substituted hydrocarbon groups such phenyl or phenyl groups substituted by one to three alkyl of 1 to 6 carbon atoms, by halogen, by hydroxy or by alkoxy of 1 to 6 carbon atoms or by a mixture thereof, or naphthyl residues.

Alkoxyalkyl refers to alkyl groups as defined earlier which are interrupted by an oxygen atom, such as methoxymethyl, methoxyethyl, ethoxyethyl, 3-(2-ethylhexyloxy)propyl etc.

Alkylene refers to alkyl groups as defined above which have an additional free valence bond, such as methylene, ethylene, 1,3-propylene, 1,2-propylene, 1,4-butylene, 1,5-pentylene, 1,6-hexylene, and 1,8-octylene.

The term poly(oxyalkylene) as used herein denotes a compound containing a polyether backbone. The polyether backbone can be based e.g. on propyleneoxide (PO), ethyleneoxide (EO) or mixed EO/PO. Examples of poly(oxyalkylene) are $-(R^9\text{-}O\text{-}R^{10})_x\text{-}O\text{-}(R^{11}\text{-}O\text{-}R^{12})_y-$, wherein R^9, R^{10}, R^{11} and R^{12} are, independently, methylene, ethylene, propylene or isopropylene, and x and y are, independently 1,2 or 3.

The compounds of the general formulas I and II above can be prepared according to procedures known in the art. Preferably, the compounds of the general formula I and II can be prepared by reacting a compound of the general formula III



(III)

wherein R^1 through R^6 have the meanings given earlier,
with a compound of the general formula IV

$$R^1\text{–}CH_2\text{–}R^2 \qquad \text{(IV)}$$

wherein R^1 and R^2 have the meanings given earlier, to yield a compound of the general formula II and, if required, reacting the compound of the formula II with a compound of the general formula V

$$R^7\text{-}NH_2 \qquad \text{(V)}$$

wherein R^7 has the meanings given earlier,
to yield a compound of the general formula I wherein m is 1 and X is R^7;

or with an α,ω-diamino-alkane, or with an α,ω-diamino-poly(oxyalkylene), e.g., a compound of the general formula VI

$$H_2N\text{-}(R^9\text{-}O\text{-}R^{10})_x\text{-}O\text{-}(R^{11}\text{-}O\text{-}R^{12})_y\text{–}NH_2 \qquad (VI)$$

wherein R^9, R^{10}, R^{11} ,R^{12}, x and y are as defined earlier,

to yield a compound of the general formula I wherein m is 2 and X is alkylene or poly(oxyalkylene).

The condensation of a compound of formula III with a compound of formula IV can be accomplished by reacting the compounds in acetic anhydride at elevated temperature such as heating to reflux and work-up of the reaction mixture by removal of the acetic anhydride, extraction of the residue with ether and chromatography. The compound of formula II can be converted into a compound of the formula I by reaction with the appropriate amine V or VI at elevated temperature, e.g. at reflux temperature of the reaction mixture. The starting compounds of formula III, V and VI are known or belong to a class of known compounds and can be prepared by methods known per se and/or described hereinafter.

The above formulae I and II encompass novel compounds which, as such, are also an object of the present invention. The novel compounds include compounds of formulae I and II wherein R^3 and R^4 are alkyl, or wherein R^3 and R^5 and/or R^4, and R^6 taken together with the carbon atoms to which they are attached, form a 5 or 6 membered ring which optionally is substituted with one to four alkyl or alkoxy groups; and compounds of formula I, wherein m is 2.

In formula I the following significances are preferred independently, collectively or in any combination or sub-combination:

(a) R^1 and R^2 are, independently, a group –CN, $COOR^8$, COR^8 or $CONR^8$ wherein R^8 is hydrogen, alkyl, cycloalkyl or aryl; e.g. R^1 and R^2 are a group –CN or R^1 is a group –CN and R^2 is a group $COOR^8$.

(b) m is 1 or 2.

(c) R^3 and R^4 are hydrogen and R^5 and R^6 are alkyl or cycloalkyl.

(d) R^7 is alkyl, cycloalkyl or alkoxyalkyl.

(e) R^2 is a group $COOR^8$ and R^8 is alkyl.

(f) X is a group $-(R^9\text{-}O\text{-}R^{10})_x\text{-}O\text{-}(R^{11}\text{-}O\text{-}R^{12})_y$ -, wherein R^9, R^{10}, R^{11} and R^{12} are, independently, methylene, ethylene or propylene, and x and y are, independently 1,2 or 3.

In formula II the following significances are preferred independently, collectively or in any combination or sub-combination:

(a) R^1 and R^2 are, independently, a group –CN, $COOR^8$, COR^8 or $CONR^8$, e.g. R^1 and R^2 are a group –CN or R^1 is a group –CN and R^2 is a group $COOR^8$.

(b) R^3 and R^4 are hydrogen and R^5 and R^6 are alkyl or cycloalkyl.

(c) R^3, R^4, R^5 and R^6 are alkyl or cycloalkyl.

Preferred compounds for use in the present invention are compounds of the formula I. From the compounds of the formula I, those wherein m is 1 and both R^1 and R^2 are a group –CN, or R^1 is a group –CN and R^2 is a group $COOR^8$, R^3 and R^4 are hydrogen, R^5 and R^6 are alkyl, and R^7 is alkyl or alkoxyalkyl are preferred. R^8 is preferably alkyl. From the compounds of the formula I, wherein m is 2 those are preferred wherein R^1 and R^2 are a group –CN, and, further, X is $-(R^9\text{-}O\text{-}R^{10})_x\text{-}O\text{-}(R^{11}\text{-}O\text{-}R^{12})_y-$, wherein R^9, R^{10}, R^{11} and R^{12}, x and y are as defined earlier.

Specifically, novel compounds included within the scope of the present invention are

2-{1-[3-(2-{2-[3-(4-dicyanomethylene-2,6-dimethyl-4H-pyridin-1-yl)-propoxy]-ethoxy}-ethoxy)-propyl]-2,6-dimethyl-1H-pyridin-4-ylidene}-malononitrile,

1-N-(2-ethylhexyl)-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

1-N-dodecyl-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

1-N-[3-(2-ethylhexyloxy)propyl]-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

1-N-[3,5,5-trimethylhexyl]-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

2-ethylhexyl (1-N-[3-(2-Ethylhexyloxy)propyl]-2,6-dimethyl-1H-pyridin-4-ylidene)cyanoacetate,

2-ethylhexyl (2,6-dimethylpyran-4-ylidene)cyanoacetate,

2-(2,6-diethyl-3,5-dimethylpyran-4-ylidene)malononitrile, and

2-(3,5-diethyl-2,6-dipropylpyran-4-ylidene)malononitrile.

The present invention also relates to compositions comprising a compound of formula I or II, formulated into a suitable support or substrate. Typically, the compositions of the invention are adopted for protecting a material that is sensitive to ultraviolet radiation, in particular solar radiation, and comprises an effective photoprotective amount of at least one of the compounds of formula I or II. In one preferred embodiment of the invention such compositions are suited for protecting the skin and/ or hair against the deleterious effects of UV-radiation. In this case, the compositions according to the invention are cosmetic compositions which comprise a topically applicable, cosmetically-acceptable vehicle,

diluent as carrier. According to another embodiment of the invention, the compounds of formula I or II can be incorporated into a plastic substrate. Compounds I and/ or II may also be used to stabilize photosensitive ingredients in topical formulations particulary colorants, such as FD&C and D&C colorants, curcumin, riboflavin, lactoflavine, tartrazine, chinolinyellow, cochenille, azorubin, amaranth, ponceau 4R, erythrosin, indigotin, chlorophylle, chlorophyllin, caramel, Carbo medicinalis, carotinoids, bixin, norbixin, annato, orlean, capsanthin, capsorubin, lycopin, xanthophylle, flavoxanthin, lutein, kryptoaxanthin, rubixanthin, violaxanthin, rhodoxanthin, canthaxanthin, betanin, anthocyans, vitamins such as vitamin A, vitamin K1, vitamin C or other active ingredients.

The compounds of formula I and II have adsorption maxima in the UV-A region. For the preparation of light screening agents, especially of preparations for dermatological and/or cosmetic use, such as skin protection and sunscreen formulations for everyday cosmetics a compound of formula I or II may be incorporated in auxiliary agents, e.g. a cosmetic base, which are conventionally used for such formulations. Where convenient, other conventional UV-A and/or UV-B screening agents, preferably a pigment, may also be added. The combination of UV filters may show a synergistic effect. The preparation of said light screening agents is well known to the skilled artisan in this field. The concentration of UV filters is varied in a wide range. For example, the amount of compounds of formula I or II and optionally an additional hydrophilic and/or lipophilic UV-A or UV-B screening agent other than the compounds of formula I or II may be in the range of from 0.5 to 12% by weight of the total composition. These additional screening agents are advantageously selected from the compounds listed below without being limited thereto:

Examples of UV B screening agents, i.e. substances having absorption maxima between about 290 and 320 nm, which come into consideration for combination with the compounds of the present invention are, e.g., the following organic and inorganic compounds:

acrylates such as 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (octocrylene, PARSOL® 340), ethyl 2-cyano-3,3-diphenylacrylate and the like;

camphor derivatives such as 4-methyl benzylidene camphor (PARSOL® 5000), 3-benzylidene camphor, camphor benzalkonium methosulfate, polyacrylamidomethyl benzylidene camphor, sulfobenzylidene camphor, sulfomethyl benzylidene camphor, therephthalidene dicamphor sulfonic acid and the like;

cinnamate derivatives such as octyl methoxycinnamate (PARSOL® MCX), ethoxyethyl methoxycinnamate, diethanolamine methoxycinnamate (PARSOL® Hydro), isoamyl methoxycinnamate and the like as well as cinnamic acid derivatives bond to siloxanes;

p-aminobenzoic acid derivatives, such as p-aminobenzoic acid, 2-ethylhexyl p-dimethylaminobenzoate, N-oxypropylenated ethyl p-aminobenzoate, glyceryl p-aminobenzoate,

benzophenones such as benzophenone-3, benzophenone-4, 2,2', 4, 4'-tetrahydroxy-benzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and the like;

esters of benzalmalonic acid such as di (2-ethylhexyl) 4-methoxybenzalmalonate;

esters of 2-(4-ethoxy anilinomethylene)propanedioic acid such as 2-(4-ethoxy anilinomethylene)propanedioic acid diethyl ester as described in EP 895,776;

organosiloxane compounds containing benzmalonate groups as described in EP 358,584, EP 538,431 and EP 709,080;

drometrizole trisiloxane (MEXORYL XL);

pigments such as microparticulated TiO_2, and the like, wherein the term "microparticulated" refers to a particle size from about 5 nm to about 200 nm, particularly from about 15 nm to about 100 nm, and which TiO_2 particles may be coated by metal oxides such as e.g. aluminum or zirconium oxides or by organic coatings such as e.g. polyols, methicones, aluminum stearate, alkyl silane;

imidazole derivatives such as e.g. 2-phenyl benzimidazole sulfonic acid and its salts (PARSOL®HS). Salts of 2-phenyl benzimidazole sulfonic acid are e.g. alkali salts such as sodium- or potassium salts, ammonium salts, morpholine salts, salts of primary, sec. and tert. amines like monoethanolamine salts, diethanolamine salts and the like;

salicylate derivatives such as isopropylbenzyl salicylate, benzyl salicylate, butyl salicylate, octyl salicylate (NEO HELIOPAN OS), isooctyl salicylate or homomenthyl salicylate (homosalate, HELIOPAN) and the like;

triazine derivatives such as octyl triazone (UVINUL T-150), dioctyl butamido triazone (UVASORB HEB), bis ethoxyphenol methoxyphenyl triazine (TINOSORB S) and the like;

encapsulated 2-ethylhexyl-4-methoxy cinnamate such as Eusolex® UV-pearls™ OMC and the like.

Examples of UV A screening agents i.e. substances having absorption maxima between about 320 and 400 nm, which come into consideration for combination with the compounds of the present invention are, e.g., the following organic and inorganic compounds:

dibenzoylmethane derivatives such as 4-tert. butyl-4'-methoxydibenzoyl-methane (PARSOL® 1789), dimethoxydibenzoylmethane, isopropyldibenzoylmethane and the like;

benzotriazole derivatives such as 2,2'-methylene-bis-(6-(2H-benzotriazole-2-yl)-4-(1,1,3,3,-tetramethylbutyl)-phenol (TINOSORB M) and the like;

phenylene-1,4-bis-benzimidazolsulfonic acids or salts such as 2,2-(1,4-phenylene)bis-(1H-benzimidazol-4,6-disulfonic acid) (NEOHELIOPAN AP);

amino substituted hydroxybenzophenones such as 2-(4-diethylamino-2-hydroxy-benzoyl)-benzoic acid hexylester as described in EP 1,046,391;

pigments such as microparticulated ZnO and the like, wherein the term "microparticulated" refers to a particle size from about 5 nm to about 200 nm, particularly from about 15 nm to about 100 nm, and which ZnO particles may be coated by metal oxides such as e.g. aluminum or zirconium oxides or by organic coatings such as e.g. polyols, methicones, aluminum stearate, alkyl silane.

As dibenzoylmethane derivatives have limited photostability it may be desirable to photostabilize these UV-A screening agents. Thus, the term "conventional UV-A screening agent" also refers to dibenzoylmethane derivatives such as e.g. PARSOL® 1789 stabilized by, e.g.,

3,3-diphenylacrylate derivatives as described in EP 514,491 and EP 780,119;

benzylidene camphor derivatives as described in US 5,605,680;

organosiloxanes containing benzmalonate groups as described in EP 358,584, EP 538,431 and EP 709,080.

The compositions of the invention may also contain usual cosmetic adjuvants and additives, such as preservatives/ antioxidants, fatty substances/ oils, water, organic solvents, silicones, thickeners, softeners, emulsifiers, additional sunscreens, antifoaming agents, moisturizers, fragrances, surfactants, fillers, sequestering agents, anionic, cationic, nonionic or amphoteric polymers or mixtures thereof, propellants, acidifying or basifying agents, dyes, colorants, pigments or nanopigments, in particular those suited for providing an additional photoprotective effect by physically blocking out ultraviolet radiation, or any other ingredients usually formulated into cosmetics, in particular for the production of sunscreen/ antisun compositions. The necessary amounts of the cosmetic and dermatological adjuvants and additives may, based on the desired product, easily be chosen by a skilled artisan in this field and will be illustrated in the examples, without being limited hereto.

An additional amount of antioxidants/ preservatives is generally preferred. All known antioxidants usually formulated into cosmetics may be used. Especially preferred are antioxi-

dants chosen from the group consisting of amino acids (e.g. glycine, histidine, tyrosine, tryptophane) and their derivatives, imidazole (e.g urocanic acid) and derivatives, peptides such as D,L-carnosine, D-carnosine, L-carnosine and derivatives (e.g. anserine), carotinoids, carotenes (e.g. α-carotene, β-carotene, lycopene) and derivatives, chlorogenic acid and derivatives, liponic acid and derivatives (e.g. dihydroliponic acid), aurothioglucose, propylthiouracil and other thiols (e.g. thioredoxine, glutathione, cysteine, cystine, cystamine and its glycosyl-, N-acetyl-, methyl-, ethyl-, propyl-, amyl-, butyl- and lauryl-, palmitoyl-; oleyl-, y-linoleyl-, cholesteryl- and glycerylester) and the salts thereof, dilaurylthiodipropionate, distearylthiodipropionate, thiodipropionic acid and its derivatives (ester, ether, peptides, lipids, nucleotides, nucleosides and salts) as well as sulfoximine compounds (such as buthionine sulfoximine, homocysteine sulfoximine, buthionine sulfone, penta-, hexa-, heptathionine sulfoximine) in very low compatible doses (e.g. pmol/kg to μmol/kg), additionally (metal)-chelators (such as α-hydroxyfatty acids, palmic-, phytinic acid, lactoferrin), α-hydroxyacids (such as citric acid, lactic acid, malic acid), huminic acid, gallic acid, gallic extracts, bilirubin, biliverdin, EDTA, EGTA and its derivatives, unsaturated fatty acids and their derivatives (such as γ-linoleic acid, linolic acid, oleic acid), folic acid and its derivatives, ubiquinone and ubiquinol and their derivatives, vitamine C and derivatives (such as ascorbyl palmitate and ascorbyl tetraisopalmitate, Mg-ascorbyl phosphate, Na-ascorbyl phosphate, ascorbyl acetate), tocopherol and derivates (such as vitamin-E-acetate, nat. vitamin E and mixtures thereof), vitamin A and derivatives (vitamin A palmitate and acetate) as well as coniferylbenzoat, rutinic acid and derivatives, α-glycosylrutin, ferulic acid, furfurylidene glucitol, butyl hydroxytoluene, butyl hydroxyanisole, trihydroxybutyrophenone, urea and its derivatives, mannose and derivatives, zinc and derivatives (e.g. ZnO, $ZnSO_4$), selenium and derivatives, (e.g. selenomethionine) stilbenes and derivatives (such as stilbenoxide, trans-stilbenoxide) and suitable derivatives (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of the named active ingredients. One or more preservatives/antioxidants may be present in an amount of about 0.01 wt.% to about 10 wt.% of the total weight of the composition of the present invention. Preferably, one or more preservatives/antioxidants are present in an amount of about 0.1 wt.% to about 1 wt.%.

Examples of emulsifiers that may be used in the present invention in order to form O/W, W/O, O/W/O or W/O/W emulsions/ microemulsions include sorbitan oleate, sorbitan sesquioleate, sorbitan isostearate, sorbitan trioleate, polyglyceryl-3-diisostearate, poly-

glycerol esters of oleic/isostearic acid, polyglyceryl-6 hexaricinolate, polyglyceryl-4-oleate, polygylceryl-4 oleate/PEG-8 propylene glycol cocoate, oleamide DEA, TEA myristate, TEA stearate, magnesium stearate, sodium stearate, potassium laurate, potassium ricinoleate, sodium cocoate, sodium tallowate, potassium castorate, sodium oleate, and mixtures thereof. Further suitable emulsifiers are phosphate esters and the salts thereof such as cetyl phosphate (Amphisol® A), diethanolamine cetyl phosphate (Amphisol®), potassium cetyl phosphate (Amphisol® K), sodium glyceryl oleate phosphate, hydrogenated vegetable glycerides phosphate and mixtures thereof. Furthermore, one or more synthetic polymers may be used as an emulsifier. For example, PVP eicosene copolymer, acrylates/C_{10-30}alkyl acrylate crosspolymer, acrylates/steareth-20 methacrylate copolymer, PEG-22/dodecyl glycol copolymer, PEG-45/dodecyl glycol copolymer, and mixtures thereof. The preferred emulsifiers are cetyl phosphate (Amphisol® A), diethanolamine cetyl phosphate (Amphisol®), potassium cetyl phosphate (Amphisol® K), PVP eicosene copolymer, acrylates/-C_{10-30}alkyl acrylate crosspolymer, PEG-20 sorbitan isostearate, sorbitan isostearate, and mixtures thereof. Emulsifiers are present in a total amount of about 0.01 wt.% to about 20 wt.% of the total weight of the composition of the present invention. Preferably, about 0.1 wt.% to about 10 wt.% of emulsifier are used.

The lipid phase may advantageously be chosen from mineral oils and mineral waxes; oils such as triglycerides of caprinic acid or caprylic acid, preferably castor oil; oils or waxes and other natural or synthetic oils, in a preferred embodiment esters of fatty acids with alcohols e.g. isopropanol, propyleneglycol, glycerin or esters of fatty alcohols with lower carboxylic acids or fatty acids; alkylbenzoates; silicone oils such as dimethylpolysiloxane, diethylpolysiloxane, diphenylpolysiloxane, cyclomethicone and mixtures thereof.

Exemplary fatty substances which may be incorporated into the oil phase of the emulsion, microemulsion, oleo gel, hydrodispersion or lipodispersion of the present invention are advantageously chosen from esters of saturated and/or unsaturated, linear or branched alkyl carboxylic acids with 3 to 30 carbon atoms, and saturated and/or unsaturated, linear and/or branched alcohols with 3 to 30 carbon atoms as well as esters of aromatic carboxylic acids and of saturated and/or unsaturated, linear or branched alcohols of 3-30 carbon atoms. Such esters may advantageously be selected from octylpalmitate, octylcocoate, octylisostearate, octyldodeceylmyristate, cetearylisononanoate, isopropylmyristate, isopropylpalmitate, isopropylstearate, isopropyloleate, n-butylstearate, n-hexyllaureate, n-decyloleat, isooctylstearate, isononylstearate, isononylisononanoate, 2-

ethyl hexylpalmitate, 2-ethylhexyllaurate, 2-hexyldecylstearate, 2-octyldodecylpalmitate, stearylheptanoate, oleyloleate, oleylerucate, erucyloleate, erucylerucate, tridecylstearate, tridecyltrimellitate, and synthetic, half-synthetic or natural mixtures of such esters e.g. jojoba oil.

Other fatty components suitable for use in the formulation of the present invention include polar oils such as lecithines and fatty acid triglycerides, namely triglycerinic esters of saturated and/or unsaturated, straight or branched carbonic acid with 8 to 24 carbon atoms, preferably of 12 to 18 carbon-atoms whereas the fatty acid triglycerides are preferably chosen from synthetic, half synthetic or natural oils (e.g. cocoglyceride, olive oil, sun flower oil, soybean oil, peanut oil, rape seed oil, sweet almond oil, palm oil, coconut oil, castor oil, hydrogenated castor oil, wheat oil, grape seed oil, macadamia nut oil and others); apolar oils such as linear and/ or branched hydrocarbons and waxes e.g. mineral oils, vaseline (petrolatum); paraffins, squalan and squalen, polyolefines, hydrogenated polyisobutenes and isohexadecanes, favored polyolefines are polydecenes; dialkyl ethers such as dicaprylylether; linear or cyclic silicone oils such as preferably cyclomethicone (octamethylcyclotetrasiloxane), cetyldimethicone, hexamethylcyclotrisiloxane, polydimethylsiloxane, poly(methylphenylsiloxane) and mixtures thereof.

Still other fatty components which may advantageously be incorporated into formulations of the present invention include isoeikosane; neopentylglycol diheptanoate; propyleneglycol dicaprylate/ dicaprate; caprylic/ capric/ diglycerylsuccinate; butyleneglycol caprylate/caprate; C_{12-15}alkyllactates; di-C_{12-15}alkyltartrates; triisostearin; dipentaerythrityl hexacaprylate/hexacaprate; propyleneglycol monoisostearate; tricaprylin; dimethylisosorbid. Especially beneficial is the use of mixtures of C_{12-15}alkylbenzoates and 2-ethylhexylisostearate, mixtures of C_{12}-C_{15}alkylbenzoates and isotridecylisononanoate as well as mixtures of C_{12-15}alkylbenzoates, 2-ethylhexylisostearate and isotridecylisononanoate.

The oily phase of the formulation of the present invention may also contain natural vegetable or animal waxes such as bee wax, china wax, bumblebee wax and other waxes of insects as well as shea butter and cocoa butter.

A moisturizing agent may be incorporated into a composition of the present invention to maintain hydration or rehydrate the skin. Moisturizers that prevent water from evaporating from the skin by providing a protective coating are called emollients. Additionally an emollient provides a softening or soothing effect on the skin surface and is generally considered safe for topical use. Preferred emollients include mineral oils, lanolin, petrolatum,

capric, caprylic triglyceraldehydes, cholesterol, silicones such as dimethicone, cyclomethicone, almond oil, jojoba oil, avocado oil, castor oil, sesame oil, sunflower oil, coconut oil and grape seed oil, cocoa butter, olive oil aloe extracts, fatty acids such as oleic and stearic, fatty alcohols such as cetyl and hexadecylalcohol, diisopropyl adipate, hydroxybenzoate esters, benzoic acid esters of C_{9-15}-alcohols, isononyl iso-nonanoate, ethers such as polyoxypropylene butyl ethers and polyoxypropylene cetyl ethers, and C_{12-15}alkyl benzoates, and mixtures thereof. The most preferred emollients are hydroxybenzoate esters, aloe vera, C_{12-15}alkyl benzoates, and mixtures thereof. An emollient may be present in an amount of about 1 wt.% to about 20 wt.% of the total weight of the composition. The preferred amount of emollient may be about 2 wt.% to about 15 wt.%, and most preferably about 4 wt.% to about 10 wt.%.

Moisturizers that bind water, thereby retaining it on the skin surface are called humectants. Suitable humectants may be incorporated into a composition of the present invention such as glycerin, polypropylene glycol, polyethylene glycol, lactic acid, pyrrolidon carboxylic acid, urea, phopholipids, collagen, elastin, ceramides, lecithin sorbitol, PEG-4, and mixtures thereof. Additional suitable moisturizers are polymeric moisturizers of the family of water soluble and/ or swellable/ and/ or with water gelating polysaccarides such as hyaluronic acid, chitosan and/or a fucose rich polysaccharide which is e.g. available as Fucogel®1000 (CAS-Nr. 178463-23-5) by SOLABIA S. One or more humectants are optionally present at about 0.5 wt.% to about 8 wt.% in a composition of the present invention, preferably about 1 wt.% to about 5 wt.%.

The aqueous phase of the compositions of the present invention may contain usual cosmetic additives such as alcohols, especially lower alcohols, preferably ethanol and/or isopropanol, low diols oder polyols and their ethers, preferably propylenglycols, glycerin, ethyleneglycol, ethyleneglycol monoethyl- or monobutyl-ether, propylene glycol-monomethyl-, monoethyl- or monobutyl ether, diethylene glycol-monomethyl-or monoethyl-ether and analogue products, polymers, foam stabilisators; electrolytes and especially one or more thickeners. Thickeners that may be used in formulations of the present invention to assist in making the consistency of a product suitable include carbomer, siliciumdioxide, magnesium and/ or aluminum silicates, beewax, stearic acid, stearyl alcohol polysaccharides and their derivatives such as xanthan gum, hydroxypropyl cellulose, polyacrylamides, acrylate crosspolymers preferably a carbopole, such as carbopole of type 980, 981, 1382, 2984, 5984 alone or mixtures thereof. Suitable neutralizing agents which may be included in the composition of the present invention to

neutralize components such as e.g. an emulsifier or a foam builder/stabilizer include but are not limited to alkali hydroxides such as a sodium and potassium hydroxide; organic bases such as diethanolamine (DEA), triethanolamine (TEA), aminomethyl propanol, and mixtures thereof; amino acids such as arginine and lysine and any combination of any foregoing. The neutralizing agent may be present in an amount of about 0.01 wt.% to about 8 wt.% in the composition of the present invention, preferably, 1 wt.% to about 5 wt.%.

The addition of electrolytes into the composition of the present invention may be necessary to change the behavior of a hydrophobic emulsifier. Thus the emulsions/ microemulsions of this invention may preferably contain electrolytes of one or several salts including anions such as a chloride, a sulfate, a carbonate, a borate or an aluminate, without being limited thereto. Other suitable electrolytes may be on the bases of organic anions such as, but not limited to, lactate, acetate, benzoate, propionate, tartrate and citrate. As cations preferably ammonia, alkylammonia, alkali or alkaline earth metals, magnesium, iron or zinc ions are selected. Especially preferred salts are potassium and sodium chloride, magnesium sulfate, zinc sulfate and mixtures thereof. Electrolytes are present in an amount of about 0.01 wt.% to about 8 wt.% in the composition of the present invention.

The cosmetic compositions of the invention are useful as compositions for photoprotecting the human epidermis or hair against the damaging effect of ultraviolet irradiation, as antisun/ sunscreen composition or as makeup product. Such compositions can, in particular, be provided in the form of a lotion, a thickened lotion, a gel, a cream, a milk, an ointment, a powder or a solid tube stick and may optionally be packaged as an aerosol and may be provided in the form of a mousse, foam or a spray. When the cosmetic composition according to the invention is provided for protecting the human epidermis against UV radiation or as antisun/ sunscreen composition, it may be in the form of a suspension or dispersion in solvents or fatty substances, or alternatively in the form of an emulsion or microemulsion (in particular of O/W or W/O type, O/W/O or W/O/W-type), such as a cream or a milk, a vesicular dispersion, in the form of an ointment, a gel, a solid tube stick or an aerosol mousse. The emulsions can also contain anionic, nonionic, cationic or amphoteric surfactants.

When the cosmetic composition according to the invention is used for protecting the hair, it may be in the form of a shampoo, a lotion, a gel or a rinse out composition, to be

applied before or after shampooing, before or after dyeing or bleaching, before, during or after permanent-waving or hair straightening operation, a styling or treatment lotion or a gel, a blow-drying or hairsetting lotion or gel, a hair lacquer, or a composition for permanent-waving, straightening, dyeing or bleaching the hair.

When the cosmetic composition according to the invention is used as makeup product for eyelashes, the eyebrows, the skin or the hair, such as an epidermal treatment cream, a foundation, a tube of lipstick, an eyeshadow, a face powder, an eyeliner, a mascara or a coloring gel, it may be solid or pasty, anhydrous or in aqueous form, such as O/W or W/O emulsion, suspension or gel.

The present invention also features formulating the compounds of formula I and II as an agent for screening out UV radiation, in particular for controlling the color of human skin.

This invention also features non-therapeutic regime/ regimen for protecting the skin and/ or hair against ultraviolet radiation, in particular solar radiation, comprising topically applying an effective amount of a cosmetic composition as described above, or of a compound of formula I or II.

Finally, this invention also features non-therapeutic regime/ regimen for controlling the variation of the color of the skin caused by ultraviolet radiation, comprising topically applying onto the skin an effective amount of a cosmetic composition as described above, or of a compound of formula I or II.

The following examples are provided to further illustrate the processes and compositions of the present invention. These examples are illustrative only and are not intended to limit the scope of the invention in any way. In the Examples, FC. means Flash chromatography; HV means high vacuum (0.1 Pa or below).

Example 1: Preparation of ethyl (2,6-dimethyl-pyran-4-ylidene) cyanoacetate

To a mixture of 9.45ml (100mmol) acetic anhydride and 1.06ml (10mmol) ethylcyano acetate 1.24g (10mmol) of 1,4-dimethyl-γ-pyrones was added. The reaction mixture was refluxed for 20h at 155°C. After evaporation of the acetic anhydride the residue was extracted with ether (2x50ml). The combined organic phases were subsequently washed with water (3x30ml) and saturated NaCl-solution (1x30ml). After drying (Na_2SO_4), the solvent was evaporated (HV) and the crude product purified via FC (n-hexane/ EtOAC 7:3) yielding 0.15g (7%) of ethyl (2,6-dimethyl-pyran-4-ylidene) cyanoacetate as a solid.

^{1}H-NMR (300MHZ, $CDCl_3$): 7.90 (*s*, 1H), 6.60 (*s*, 1H), 4.2 (*q*, 2H, $-OCH_2$), 2.29 (*s*, 6H, CH_3), 1.32 (*t*, 3H, CH_3). MS (EI): 219 (100, M^+), 191 (13), 174 (83), 147 (64), 122 (9), 91 (4), 43 (11), 29 (3). IR (neat): 2987*w*, 2193*s*, 1697*s*, 1649*vs*, 1582*s*, 1513*s*, 1459*m*, 1407*m*, 1390*w*, 1362*m*, 1338*s*, 1251*vs (br.)*, 1212*s*, 1173*s*, 1135*s*, 1059*m*, 1025*m* cm^{-1}. M.p.: 163-164°C, UV: λ_{max}= 348nm (ε = 24'982).

Example 2: Preparation of 2-ethylhexyl (2,6-dimethyl-pyran-4-ylidene) cyanoacetate

To a suspension of 1.72g (10mmol) of (2,6-dimethyl-4H-pyran-4-ylidene)malononitril in 33ml of 2-ethyl-1-hexanol, 3.3ml of water and 3.3ml of concentrated H_2SO_4 were added. The reaction mixture was refluxed at 100°C for 48h. After addition of 50 ml of water the resulting solution was extracted with with ether (2x100ml). The organic phase was washed with water (2x50ml) and with saturated NaCl-solution (1x50ml). After drying (Na_2SO_4), the solvent was evaporated (HV) and the crude product was purified via FC (n-hexane/ EtOAC 85:15) yielding 1.71g (56%) of 2-ethylhexyl (2,6-dimethyl-pyran-4-ylidene) cyano-acetate as a slightly yellow solid.

^{1}H-NMR (300MHZ, $CDCl_3$): 7.90 (*s*, 1H), 6.60 (*s*, 1H), 4.08 (*m*, 2H, $-OCH_2$), 2.29 (*s*, 6H, CH_3), 1.65 (*m*, 1H), 1.50-1.20 (*m*, 8H), 0.90 (*m*, 6H, $2CH_3$). MS (EI): 303 (28, M^+), 191 (100), 174 (41), 147 (27). IR (neat): 2958*m*, 2931*m*, 2873*w*, 2198*m*, 1696*s*, 1656*vs*, 1585*m*, 1523*s*, 1459*m*, 1410*m*, 1379*w*, 1341*s*, 1274*m*, 1252*s (br.)*, 1213*m*, 1176*m*, 1131*m*, 1062m, 1038*w* cm^{-1}. M.p.: 64-65°C, UV: λ_{max}= 352nm (ε = 25'548).

Example 3: Preparation of 2-(2,6-diethyl-3,5-dimethylpyran-4-ylidene)malononitrile

To a solution of 0.33g (5mmol) of malonodinitrile in 2.4ml (25mmol) acetic anhydride 1.20g (5mmol) of 2,6-diethyl-3,5-dipropyl-pyran-4-one (prepared according to J. Chem. Soc (C), 1967, 828-830) was added. After addition of 150 ml of water the resulting solution was extracted twice with ether (50ml). The combined organic phases were washed with water (2x50ml) and with saturated NaCl-solution (1x30ml). After drying (Na_2SO_4), the solvent was evaporated (HV) and the crude product was purified via FC (n-hexane/ EtOAC 7:3) yielding 0.54g (47%) of 2-(2,6-diethyl-3,5-dimethylpyran-4-ylidene)malono-nitrile as a brown solid.

^{1}H-NMR (300MHZ, $CDCl_3$): 2.64 (*q*, 4H, $2CH_2$), 2.35 (*s*, 6H, $2CH_3$) 1.21 (*s*, 6H, $2CH_3$). MS (EI): 228 (100, M^+), 213 (3), 201 (5), 200 (5),188 (48), 163 (9), 57 (8), 43 (3), 29 (4). IR (neat): 2986*m*, 2942*m*, 2343*w (br.)*, 2193*s*, 1622*vs*, 1551*s*, 1428*s (br.)*, 1387*s*, 1203*m*, 1189*s*, 1169*s*, 1082*m*, 1033*s* cm^{-1}. M.p.: 64-65°C, UV: λ_{max}= 366nm (ε = 22'808).

Example 4: Preparation of 2-(3,5-diethyl-2,6-dipropylpyran-4-ylidene)malononitrile

2-(3,5-Diethyl-2,6-dipropylpyran-4-ylidene)malononitrile was prepared in analogy to the procedure of example 3.

^{1}H-NMR (300MHZ, $CDCl_3$): 2.90 (*q*, 4H, $2CH_2$) 2.60 (*t*, 4H, $2CH_2$), 1.70 (*m*, 2H, $2CH_2$), 1.22 (*t*, 6H, $2CH_3$) 1.00 (*t*, 6H, $2CH_3$). MS (EI): 284 (54, M^+), 269 (100), 256 (10), 244 (18), 230 (9), 216 (9), 203 (7), 71 (3), 43 (10). IR (neat): 2965*m*, 2934*w*, 2875*w*, 2198*s*, 1615*vs*, 1550*w*, 1443*s (br.)*, 1379*m*, 1325*w*, 1255*w*, 1178*m*, 1155*m*, 1055*m*, 956*m* cm^{-1}, UV: λ_{max}= 364nm (ε = 21'729).

Example 5: Preparation of 1-N-(2-ethylhexyl)-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine

A solution of 0.5g (2.9mmol) of (2,6-dimethyl-4H-pyran-4-ylidene)malononitril in 7.6ml (6g, 46.4mmol) 2-ethyl-1-hexylamine was refluxed for 1h under nitrogen. Removal of the excess of ethyl-1-hexylamine at reduced pressure left a solid which was recrystallized from 15ml EtOAc/ MeOH 2/1 yielding 0.45g (55%) of 1-N-(2-ethylhexyl)-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine.

^{1}H-NMR (300MHZ, $CDCl_3$): 6.7 (*s*, 2H, H-C(3), H-C(5)), 3.85 (*d*, 2H, H-C(1')), 2.42 (*s*, 6H, $-CH_3$), 1.7 (m, 1H, H-C(2')), 1.41-1.12 (*m*, 8H, CH_2), 0.9 (*2t*, 6H, $2CH_3$). MS (CI): 284.3 ($M+H^+$). IR (neat): 2966*m*, 2932*m*, 2860*w*, 2187*s*, 2164*vs*, 1638*vs*, 1552*s*, 1499*s*, 1469*m*, 1372*s*, 1347*s*, 1221*m*, 1185*s*, 1067*m*, 1036*w* cm^{-1}. M.p.: 187°C, UV: λ_{max}= 372nm (ε = 39'687).

Example 6: Preparation of Compounds in analogy to Example 1

In analogy to the procedure of Example 1, the following compounds were obtained:

1-N-dodecyl-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine.

^{1}H-NMR (300MHZ, $CDCl_3$): 6.69 (*s*, 2H, H-C(3), H-C(5)), 3.88 (*m*, 2H, H-C(1')), 2.45 (*s*, 6H, $-CH_3$), 1.68 (m, 2H, H-C(2')), 1.45-1.20 (*m*, 19H, CH_2), 0.88 (*t*, 3H,$-CH_3$). MS (EI): 339 (M^+,100), 324 (73), 310 (13), 296(10), 282(12), 268 (10), 254 (13), 240 (8), 226 (6), 212 (7), 198 (8), 185 (14), 171 (27), 57 (10), 43 (15). IR (neat): 2914*vs*, 2851*vs*, 2189*vs*, 2163*vs*, 1644*vs*, 1554*s*, 1504*m*, 1472*s*, 1359*s*, 1314*m*, 1223*m*, 1188*s*, 1127*w*, 1069*m*, 1037*w* cm^{-1}. M.p.: 161-162°C. UV: λ_{max}= 370nm (ε = 42'538).

1-N-[3-(2-ethylhexyloxy)propyl]-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine.

^{1}H-NMR (300MHZ, $CDCl_3$): 6.69 (*s*, 2H, H-C(3), H-C(5)), 4.05 (*m*, 2H, H-C(1')), 3.46 (*t*, 2H, H-C(3'), 3.31 (*d*, 2H, H-C(1''), 2.48 (*s*, 6H, $-CH_3$), 1.93 (*m*, 2H, H-C(2')), 1.50 (m, 2H, H-C(2'')), 1.40-1.20 (*m*, 8H, CH_2), 0.90 (2*t*, 6H, $2CH_3$). MS (CI): 342 ($M+H^+$). IR (neat): 2957*m*, 2928*m*, 2858*m*, 2189*vs*, 2163*vs*, 1644*vs*, 1553*s*, 1503*m*, 1482*m*, 1461*m*, 1379*m*, 1356*vs*, 1312*w*, 1223*w*, 1191*s*, 1107*s (br.)*, 1068*m*, 1037*m* cm^{-1}. M.p.: 116-117°C. UV: λ_{max}= 370nm (ε = 37'846).

1-N-[3,5,5-trimethylhexyl]-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine.
^{1}H-NMR (300MHZ, $CDCl_3$): 6.62 (*s*, 2H, H-C(3), H-C(5)), 3.9 (*m*, 2H, H-C(1')), 2.49 (*s*, 6H, $-CH_3$), 1.70 (*m*, 2H, H-C(2')), 1.55 (m, 2H, H-C(3')), 1.20 (*m*, 2H, H-C(4')), 1.05 (*d*, 2H, CH_3), 0.92 (*s*, 9H, $3CH_3$). MS (CI): 298 ($M+H^+$). IR (neat): 2954*m*, 2192*vs*, 2171*vs*, 1626*vs*, 1554*m*, 1503*m*, 1481*m*, 1422*w*, 1388*m*, 1344*vs*, , 1224*w*, 1189*s*, 1107*s*, 1069*m*, 1036*m* cm^{-1}. M.p.: 236-237-117°C. UV: λ_{max}= 372nm (ε = 39'569).

1-N-methyl-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine.
^{1}H-NMR (300MHZ, $CDCl_3$): 6.65 (*s*, 2H, H-C(3), H-C(5)), 3.61 (*s*, 3H, $-NCH_3$), 2.49 (*s*, 6H, $-CH_3$). MS (EI): 185 (M^+). IR (neat): 2962*w*, 2185*vs*, 2161*vs*, 1635*vs*, 1555*s*, 1495*s*, 1422*m*, 1383*m*, 1354*vs*, , 1223*w*, 1195*s*, 1067*s*, 1038*m* cm^{-1}. M.p.: >250°C. UV: λ_{max}= 368nm (ε = 36'280).

1-N-butyl-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine.
^{1}H-NMR (300MHZ, $CDCl_3$): 6.65 (*s*, 2H, H-C(3), H-C(5)), 3.90 (*m*, 2H, H-C(1')), 2.49 (*s*, 6H, $-CH_3$), 1.69 (*m*, 2H, H-C(2')), 1.45 (*m*, 2H, H-C(3')), 1.005 (*s*, 3H, $-CH_3$). MS (CI): 228 ($M+H^+$). IR (neat): 2956*w*, 2869*w*, 2191*vs*, 2167*vs*, 1633*vs*, 1553*s*, 1499*s*, 1479*m*, 1383*m*, 1361*vs*, 1338*s*, 1223*m*, 1185*s*, 1112*m*, 1067*s* cm^{-1}. M.p.: 198°C. UV: λ_{max}= 370nm (ε = 37'300).

Example 7: Preparation of 2-ethylhexyl (1-N-butyl-2,6-dimethyl-1H-pyridin-4-ylidene)cyanoacetate

A solution of 0.30g (1mmol) of 2-ethylhexyl (2,6-dimethyl-pyran-4-ylidene)cyanoacetate (prepared as described in example 1) in 4ml butylamine was refluxed at 80°C for 1h under nitrogen. Removal of the excess of butylamine at reduced pressure left a orange oil which was purified by FC (n-hexane/EtOAc 1:1) yielding 0.23g (64%) of 2-ethylhexyl (1-N-butyl-2,6-dimethyl-1H-pyridin-4-ylidene)cyanoacetate as a slightly yellow solid.

^{1}H-NMR (300MHZ, $CDCl_3$): 8.20 (*s*, 1H), 6.86 (*s*, 1H), 4.05 (*m*, 2H, $-OCH_2$), 3.85 (*t*, 2H, $-NCH_2$) 2.45 (*s*, 6H, CH_3), 1.65 (*m*, 3H), 1.50-1.20 (*m*, 10H), 1.01 (*t*, 3H, CH_3), 0.9 (*m*, 6H, $2CH_3$). MS (CI): 359 ($M+H^+$). IR (neat): 2960*m*, 2929*m*, 2858*w*, 2177*vs*, 1665*vs*, 1619*vs*, 1546*m*, 1501*s*, 1479*s*, 1380*s*, 1354*s*, 1316*m*, 1252*s*, 1190*m*, 1114*m*, 1056*s (br.)* cm^{-1}. M.p.: 69-70°C, UV: λ_{max}= 374nm (ε = 39'654)

Example 8: Preparation of 2-ethylhexyl (1-N-[3-(2-ethylhexyloxy)propyl]-2,6-dimethyl-1H-pyridin-4-ylidene)cyanoacetate

In analogy to Example 11 there was obtained 2-ethylhexyl (1-N-[3-(2-ethylhexyloxy)-propyl]-2,6-dimethyl-1H-pyridin-4-ylidene)cyanoacetate.

^{1}H-NMR (300MHZ, $CDCl_3$): 8.20 (*s*, 1H), 6.85 (*s*, 1H), 4.05 (*m*, 2H, $-NCH_2$, $-OCH_2$), 3.46 (*t* ,2H, $-OCH_2$), 3.31 (*d*, 2H, CH_2), 2.45 (*s*, 6H, CH_3), 1.90 (*m*, 2H), 1.65 (*m*, 1H), 1.52-1.20 (*m*, 17H), 0.89 (*m*, 12H, $4CH_3$), 0.9 (*m*, 6H, $2CH_3$). MS (CI): 473 ($M+H^+$). IR (neat): 2958*m*, 2926*m*, 2858*m*, 2179*m*, 1671*s*, 1620*vs*, 1547Iml, 1503*m*, 1483*s*, 1375*m*, 1349*s*, 1307*m*, 1253*vs*, 1188*m*, 1103*s*, 1053*vs*, cm^{-1}. M.p.: 69-70°C, UV: λ_{max}= 366nm (ε = 46'163).

Example 9: Preparation of 2-{1-[3-(2-{2-[3-(4-dicyanomethylene-2,6-dimethyl-4H-pyridin-1-yl)-propoxy]-ethoxy}-ethoxy)-propyl]-2,6-dimethyl-1H-pyridin-4-ylidene}-malononitrile

A solution of 0.52g (3mmol) of (2,6-dimethyl-4H-pyran-4-ylidene)malononitril and 0.3ml (1.5mmol) of 4,7,10-trioxa-1,13-tridecanediamine in 6ml of acetontrile was heated to 90°C for 70h under nitrogen. Removal of the acetonitrile left a brown residue which was re-crystallized from 25ml methanol and 10ml ethyl acetate yielding 0.68g (43%) of 2-{1-[3-(2-{2-[3-(4-dicyanomethylene-2,6-dimethyl-4H-pyridin-1-yl)-propoxy]-ethoxy}-ethoxy)-propyl]-2,6-dimethyl-1H-pyridin-4-ylidene}-malononitrile.

^{1}H-NMR (300MHZ, $CDCl_3$): 6.62 (*s*, 4H, H-C(3), H-C(5)), 4.10 (*m*, 4H, H-C(1')), 3.62 (*s*, 8H, $-OCH_2CH_2O-$), 3.55 (*t*, 4H, H-C(3')), 2.50 (*s*, 6H, $-CH_3$), 2.00 (*m*, 4H, H-C(2')). MS (CI): 529 ($M+H^+$). IR (neat): 3521*w(br.)*, 2868*w*, 2191*s*, 2163*s*, 1648*vs*, 1553*s*, 1504*m*, 1484*w*, 1380*w*, 1357*s*, 1313*w*, 1223*w*, 1192*m*, 1102*m (br.)*, 1070*m*, 1037*m* cm^{-1}. M.p.: 138-139°C, UV: λ_{max}= 372nm (ε = 67'608).

Example 10: Preparation of an oil-in-water sun milk

An oil-in-water sun milk can be prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w
A	Compound of formula I or II		0.1-25
	Lanette O	Cetearyl Alcohol	2.00
	Myritol 318	Caprylic/capric Triglyceride	6.00
	Mineral oil	Mineral oil	2.00
	Vitamin E acetate	Tocopheryl Acetate	1.00
	Prisorine 3515	Isostearyl Alcohol	4.00
	Edeta BD	Disodium EDTA	0.10
	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben	0.60
	AMPHISOL K	Potassium Cetyl Phosphate	2.00
B	Water deionized	Aqua	ad 100
	1,2-Propylen Glycol	Propylene Glycol	5.00
	Carbopol 981	Carbomer	0.30
C	KOH 10% solution	Potassium Hydroxyde	2.10

Procedure: Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring. Then add part C). Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring.

Example 11: Preparation of an oil-in-water sun milk with pigments

An oil-in-water sun milk with pigments is prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w/w
A	PARSOL SLX	Dimethico Diethylbenzalmalonate	6.00
	Compound of formula I or II		0.1-25
	Neo Heliopan AP	2,2-(1,4-phenylene)bis-(1H-benzimidazol-4,6-disulfonic acid)	3.00
	Tinosorb S	2,4-Bis((4-(ethyl-hexylox)-2-hydroxy)-phenyl)-6-(4-methoxyphenyl)-1,3,5-triazine	3.00
	Lanette O	Cetearyl Alcohol	2.00

	Myritol 318	Caprylic/capric Triglyceride	6.00
	Mineral oil	Mineral oil	2.00
	Vitamin E acetate	Tocopheryl Acetate	1.00
	Prisorine 3515	Isostearyl Alcohol	4.00
	Edeta BD	Disodium EDTA	0.10
	Phenonip	Phenoxyethanol & Methylparaben & Ethyl-paraben & Propylparaben & Butylparaben	0.60
	AMPHISOL K	Potassium Cetyl Phosphate	2.00
B	Water deionized	Aqua	ad100
	1,2-Propylen Glycol	Propylene Glycol	5.00
	Carbopol 981	Carbomer	0.30
	Tinosorb M	Methylene Bis-Benzotriazolyl Tetramethyl-butylphenol	6.00
C	KOH 10% solution	Potassium Hydroxyde	2.10

Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring Then add part C). Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring.

Example 12: Preparation of a water-resistant sun milk

A water-resistant sun milk is prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w
A	PARSOL SLX	Dimethico Diethylbenzalmalonate	6.00
	PARSOL 1789	Butyl Methoxydibenzoylmethane	2.00
	Compound of formula I or II		0.1-25%
	Parsol 5000	4-Methylbenzylidene Camphor	4.00
	Parsol MCX	Ethylhexylmethoxycinnamate	6.00
	Uvinul T 150	Ethylhexyltriazone	2.00
	Silicone DC 200/350 cs	Dimethicone	1.00
	Lanette O	Cetearyl Alcohol	2.00
	Softisan 100	Hydrogenated Coco-Glycerides	3.00

	Tegosoft TN	C12-15 Alkyl Benzoate	6.00
	Cetiol B	Dibutyl Adipate	7.00
	Vitamin E acetate	Tocopheryl Acetate	2.00
	Berkemyol (Grape Seed)	Palmitoyl Grape seed Extract	1.00
	BHT	BHT	0.05
	Edeta BD	Disodium EDTA	0.10
	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben	0.60
	AMPHISOL	Cetyl Phosphate DEA	2.00
B	Water deionized	Aqua	ad 100
	Propylene Glycol	Propylene Glycol	5.00
	Carbopol 980	Carbomer	0.30
C	KOH (10% sol.)	Potassium Hydroxide	1.50

Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring Then add part C). Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring.

Example 13: Preparation of a sun milk for babies and children

A sun milk for babies and children is prepared with the followiung ingredients

	Ingredients	INCI Nomenclature	% w / w
A	Compound of formula I or II		0.1-25
	Titanium Dioxide	Titanium Dioxide microfine	4.00
	Tegosoft TN	C12-15 Alkyl Benzoate	5.00
	Silicone 2503 Cosmetic Wax	Stearyl Dimethicone	2.00
	Cetyl Alcohol	Cetyl Alcohol	1.00
	Butylated Hydroxytoluene	BHT	0.05
	Estol GMM 3650	Glyceryl Myristate	4.00
	Edeta BD	Disodium EDTA	0.10
	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben &	0.60

		Butylparaben	
	AMPHISOL A	Cetyl Phosphate	2.00
B	Water deionized	Aqua	ad 100
	Carbopol 980	Carbomer	10.00
	Glycerine	Glycerine	3.00
C	KOH sol. 10%	Potassium Hydroxide	0.50

Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring Then add part C). Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring.

Example 14: Preparation of a high protective sun milk

A high protective sun milk is prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w
A	PARSOL SLX	Dimethico Diethylbenzalmalonate	6.00
	PARSOL 1789	Butyl Methoxydibenzoylmethane	2.00
	Compound of formula I or II		0.1-25%
	Parsol 5000	4-Methylbenzylidene Camphor	4.00
	Parsol MCX	Ethylhexylmethoxicinnamate	6.00
	Uvinul T 150	Ethylhexyl Triazone	2.00
	Silicone DC 200/350 cs	Dimethicone	1.00
	Lanette O	Cetearyl Alcohol	2.00
	Softisan 100	Hydrogenated Coco-Glycerides	3.00
	Tegosoft TN	C12-15 Alkyl Benzoate	6.00
	Cetiol B	Dibutyl Adipate	7.00
	Vitamin E acetate	Tocopheryl Acetate	2.00
	Berkemyol (Grape Seed)	Palmitoyl Grape seed Extract	1.00
	BHT	BHT	0.05
	Edeta BD	Disodium EDTA	0.10
	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben	0.60
	AMPHISOL K	Potassium Cetyl Phosphate	2.00

B	Water deionized	Aqua	ad 100
	Propylene Glycol	Propylene Glycol	5.00
	Carbopol 980	Carbomer	0.30
C	KOH (10% sol.)	Potassium Hydroxide	1.50

Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring Then add part C). Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring.

Example 15: Preparation of a water-free sun gel

A water-free sun gel is prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w
A	PARSOL MCX	Ethylhexyl Methoxycinnamate	6.00
	PARSOL 1789	Butyl Methoxydibenzoylmethane	4.00
	PARSOL 5000	4-Methylbenzylidene Camphor	4.00
	Compound of formula I or II		0.1-25%
	Uvasorb HEB	Diethylhexyl Butamido Triazone	1.50
	Vitamin E acetate	Tocopheryl Acetate	1.50
	Tegosoft TN	C12-15 Alkyl Benzoate	9.00
	Elefac I-205	Ethylhexyldodecyl Neopentanoate	2.00
	Alcohol	Alcohol	ad 100.00
	Isopropyl Alcohol	Isopropyl Alcohol	20.00
B	Klucel MF	Hydroxypropylcellulose	2.00

Heat part A) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to ambient temperature while stirring.

Example 16: Preparation of a sun gel

A sun gel is prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w

A	Pemulen TR-2	Acrylates/C10-30 Alky Acrylate Crosspolymer	0.60
	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben	0.60
	Edeta BD	Disodium EDTA	0.1
	Aqua	Aqua	ad 100
	Compound of formula I or II		0.01-25
B	PARSOL MCX	Ethylhexyl Methoxycinnamate	5.00
	PARSOL 1789	Butyl Methoxydibenzoylmethane	4.00
	PARSOL 340	Octocrylene	3.00
	Tegosoft TN	C12-15 Alkyl Benzoate	15.00
	Antaron V-216	PVP/Hexadecene Copolymer	1.00
	Vitamin E acetate	Tocopheryl Acetate	0.50
	Uvinul TiO2	Titanium Dioxide and Trimethoxycaprylylsilane	5.00
	Butylated Hydroxytoluene	BHT	0.05
	Cremophor RH 410	PEG-40 Hydrogenated Castor Oil	0.50
C	Tris Amino	Tromethamine	0.50
D	Parfum	Parfum	q.s.

Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring. Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring. Then add part C) and D).

Example 17: Preparation of a high protection water-in-oil sun milk

A high protection water-in-oil sun milk is prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w
A	PARSOL MCX	Ethylhexyl Methoxycinnamate	6.00
	PARSOL 1789	Butyl Methoxydibenzoylmethane	2.00
	PARSOL 5000	4-Methylbenzylidene Camphor	4.00
	Uvinul T 150	Ethylhexyl Triazone	2.00

	Uvinul TiO2	Titanium Dioxide and Trimethoxycaprylylsilane	5.00
	Compound of formula I or II		0.1-25
	Arlacel P 135	PEG-30 Dipolyhydroxystearate	2.00
	Tegosoft TN	C12-15 Alkyl Benzoate	5.00
	Cosmacol EMI	Di-C12-13 Alkyl Malate	6.00
	Miglyol 840	Propylene Glycol Dicaprylate/Dicaprate	6.00
	Butylated Hydroxytoluene	BHT	0.05
	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben	0.60
B	Deionized water	Aqua	ad 100
	Glycerin	Glycerin	5.00
	Edeta	Disodium EDTA	0.1
	NaCl	Sodium Chloride	0.30
C	Parsol HS	Phenylbenzyimidazole Sulphonic Acid	4.00
	Water	Aqua	20.00
	Triethanolamine 99%.	Triethanolamine	2.50

Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring Then add part C). Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring.

Example 18: Preparation of a water-in-oil milk with pigments

A water-in-oil milk with pigments can be prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w
A	Cremophor WO 7	PEG-7 Hydrogenated Castor Oil	6.00
	Elfacos ST 9	PEG-45/Dodecyl Glycol Copolymer	2.00
	Parsol MCX	Ethylhexyl Methoxycinnamate	5.00
	Parsol 1789	Butyl Methoxydibenzoylmethane	3.00
	Compound of formula I or II		0.1-25
	Tinosorb S	2,4-Bis((4-(ethyl-hexylox)-2-hydroxy)-	3.00

		phenyl)-6-(4-methoxyphenyl)-1,3,5-triazine	
	Parsol 5000	4-Methylbenzylidene Camphor	4.00
	Uvinul TiO2	Titanium Dioxide and Trimethoxycaprylylsilane	2.00
	Microcrystalline wax	Microcrystalline Wax	2.00
	Miglyol 812	Caprylic/capric Triglyceride	5.00
	Vitamin E acetate	Tocopheryl Acetate	1.00
	Jojoba oil	Simmondsia Chinensis Seed Oil	5.00
	Edeta BD	Disodium EDTA	0.10
	Butylated Hydroxytoluene	BHT	0.05
	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben	0.60
B	Water deionized	Aqua	ad 100
	Glycerin	Glycerin	5.00
C	Neo Heliopan AP		2.00
	Water deionized	Aqua	20.00
	KOH 10% solution	Potassium Hydroxide	4.00

Procedure : Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring. Then add part C). Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring.

Example 19: Preparation of a hair conditioner

A hair conditioner can be prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w
A	Lanette O	Cetearyl Alcohol	3.00
	Cetiol LC	Coco Caprylate / Caprate	2.50
	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben	0.60

	Cremophor A6	Ceteareth-6 & Stearyl Alcohol	2.00
	Cremophor A25	Ceteareth-25	2.00
	Compound of formula I or II		0.1-25
B	Parsol SLX	Dimethico-diethylbenzalmalonate	1.00
	Tween 80	Polysorbate 80	q.s.
C	Water	Aqua	ad. 100
	EDETA BD	Disodium EDTA	0.20
	Carbopol 980	Carbomer	0.20
D	Panthenol 75%	Panthenol	0.50
E	Triethanolamine	Triethanolamine	q.s.
			100

Procedure: Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring. Add part C). Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring. Then add parts D) and E).

Example 20: Preparation of a protective Day cream with Vitamin C

A protective Day cream with Vitamin C can be prepared with the following ingredients

	Ingredients	INCI Nomenclature	% w / w
A	PARSOL SLX	Dimethico Diethylbenzalmalonate	4.00
	PARSOL 1789	Butyl Methoxydibenzoylmethane	1.50
	Glyceryl Myristate	Glyceryl Myristate	2.00
	Compound of formula I or II		0.1-25
	Cetyl Alcohol	Cetyl Alcohol	0.50
	Myritol 318	Caprylic/Capric Triglyceride	5.00
	Crodamol DA	Diisopropyl Adipate	5.00
	Vitamin E acetate	Tocopheryl Acetate	2.00
	Butylated Hydroxytoluene	BHT	0.05

	Phenonip	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben & Butylparaben	0.60
	Edeta BD	Disodium EDTA	0.10
	AMPHISOL K	Potassium Cetyl Phosphate	2.00
B	Water deionized	Aqua	ad 100
	1,2-Propylene Glycol	Propylene Glycol	2.00
	D-PANTHENOL 75 L	Panthenol	2.00
	Ethanol	Ethanol	5.00
	Allantoin	Allantoin	0.20
	Carbopol ETD 2001	Carbomer	0.30
C	KOH 10% sol.	Potassium Hydroxide	1.50
D	Water	Aqua	10.00
	STAY-C 50	Sodium Ascorbyl Phosphate	0.50
E	Perfume	Perfume	q.s.

Procedure : Heat part A) and B) to 85°C while stirring. When homogeneous, add part B) to A) under agitation. Cool to about 45°C while stirring. Add part C).. Homogenize at 11000 rpm to achieve a small particle size. Cool to ambient temperature while stirring. Then add parts D) and E).

Example 21: Preparation of a pearly shampoo

A pearly shampoo with Parsol SLX and Phytantriol and the following ingredients can be prepared as follows

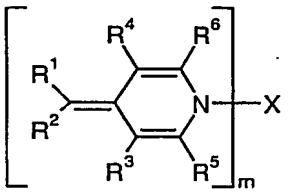
	Ingredients	INCI Nomenclature	% w / w
A	Texapon NSO-BZ	Sodium Laureth Sulfate	50.00
	Carbopol Aqua SF-1	Acrylates Copolymer	7.00
	Parsol SLX	Polysilicone-15	1.00
	Kathon CG	Methylchloroisothiazolinone and Methyl-	0.10

		isothiazolinone	
	D-Panthenol 75 L	Panthenol	0.50
	Deionized Water	Aqua	27.40
B	NaOH 30%	Sodium Hydroxide	1.10
C	Compound of formula I or II		0.1-25
	Cetiol HE	PEG-7 Glyceryl Cocoate	1.00
	Tego Betaine L	Cocamidopropyl Betaine	5.00
	Euperlan PK-3000 OK	Glycol Distearate and Glycerine and Laureth-4 and Cocamidopropyl Betaine	3.00
	EDETA BD	Disodium EDTA	0.20
	FD&C Blue No.1, 1,0% sol.	CI 42090	0.01
	Natrium Chloride	Sodium Chloride	0.50
D	Cremophor RH 40	PEG-40 Hydrogenated Castor Oil	2.00
	Phytantriol	Phytantriol	0.20
	Perfume	Perfume	1.00

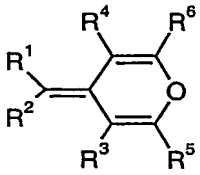
Procedure: Part A: Add all the ingredients and mix under slow agitation. Neutralize Part A with Part B until a pH of 6.5 is reached. Part C: Add all the ingredients to AB and mix under slow agitation. Mix Part D together, and add it to ABC under moderate agitation.

What is claimed is :

1. A UV-A screening composition comprising a compound of the general formula I or II



(I)



(II)

wherein

m is 1 or 2;

R^1 and R^2 are identical or different electron-withdrawing groups, or one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is an electron-withdrawing group;

R^3, R^4, R^5, are R^6 are, independently, hydrogen, alkyl, cycloalkyl or aryl;

R^3 and R^5 and/or R^4, and R^6 taken together with the carbon atoms to which they are attached, form a 5 or 6 membered ring which is optionally substituted with one to four alkyl, cycloalkyl or alkoxy groups;

X is a moiety R^7, when m is 1; and is alkylene or poly(oxyalkylene) when m is 2; and

R^7 is hydrogen, alkyl, cycloalkyl, alkoxyalkyl or aryl.

2. A composition according to claim 1, wherein the compound of formula I is selected from

1-N-(2-ethylhexyl)-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

1-N-dodecyl-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

1-N-[3-(2-ethylhexyloxy)propyl]-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

1-N-[3,5,5-trimethylhexyl]-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

1-N-methyl-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

1-N-butyl-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine,

2-ethylhexyl (1-Butyl-2,6-dimethyl-1H-pyridin-4-ylidene)cyanoacetate,

2-{1-[3-(2-{2-[3-(4-dicyanomethylene-2,6-dimethyl-4H-pyridin-1-yl)-propoxy]-ethoxy}-ethoxy)-propyl]-2,6-dimethyl-1H-pyridin-4-ylidene}-malononitrile, and

2-ethylhexyl (1-N-[3-(2-Ethylhexyloxy)propyl]-2,6-dimethyl-1H-pyridin-4-ylidene)cyanoacetate.

3. A composition according to claim 1, wherein the compound of formula II is selected from ethyl (2,6-dimethyl-pyran-4-ylidene) cyanoacetate,

2-ethylhexyl (2,6-dimethyl-pyran-4-ylidene)cyanoacetate,
2-(2,6-diethyl-3,5-dimethylpyran-4-ylidene)malononitrile and
2-(3,5-diethyl-2,6-dipropylpyran-4-ylidene)malononitrile.

4. A composition as in any one of claims 1 to 3 comprising from 0.5 % by weight to 12 % by weight of a compound of formula I or II.

5. A composition as in any one of claims 1 to 3 wherein additionally a further UV-A screening agent and/or UV-B screening agent is present.

6. A composition as in any one of claims 1 to 4 for protecting human skin or hair which comprises a topically applicable, cosmetically acceptable carrier or for protecting photo-instable ingredients in a topically applicable cosmetically acceptable carrier.

7. A composition as in any one of claims 1 to 4 wherein the compound of formula I or II is incorporated into a plastic substrate.

8. The use of a compound of formula I or II as defined in claim 1 as a UV-A screening agent, particularly for protecting human skin or hair.

9. A compound of the general formula I or II according to claim 1 wherein R^3 and R^4 are alkyl, or wherein R^3 and R^5 and/or R^4, and R^6 taken together with the carbon atoms to which they are attached, form a 5 or 6 membered ring which optionally is substituted with one to four alkyl or alkoxy groups.

10. A compound of the general formula I according to claim 1 wherein m is 2.

11. A compound of formula I or II according to claim 1 selected from
2-{1-[3-(2-{2-[3-(4-dicyanomethylene-2,6-dimethyl-4H-pyridin-1-yl)-propoxy]-ethoxy}-ethoxy)-propyl]-2,6-dimethyl-1H-pyridin-4-ylidene}-malononitrile;
1-N-(2-ethylhexyl)-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine;
1-N-dodecyl-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine;
1-N-[3-(2-ethylhexyloxy)propyl]-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine;
1-N-[3,5,5-trimethylhexyl]-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine;
2-ethylhexyl (2,6-dimethyl-pyran-4-ylidene)cyanoacetate;
2-ethylhexyl (1-N-[3-(2-Ethylhexyloxy)propyl]-2,6-dimethyl-1H-pyridin-4-ylidene)cyanoacetate;
2-(2,6-diethyl-3,5-dimethylpyran-4-ylidene)malononitrile; and

2-(3,5-diethyl-2,6-dipropylpyran-4-ylidene)malononitrile.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/01049

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/42 A61Q17/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KLEMM, L. H. ET AL: "Chemistry of thienopyridines. XLII. Three novel compounds derived from thienopyridine N-oxides '1!" JOURNAL OF HETEROCYCLIC CHEMISTRY (1994), 31(1), 161-3 , XP009011732 Compound a (tautomerism 7) Compound a (tautomerism 9) --- -/--	9

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 June 2003	18/06/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Goss, I

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/01049

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	KLEMM, L. H. ET AL: "Chemistry of thienopyridines. XXXV. Synthesis, tautomerism, and reactions of quinoline and thienopyridine systems which bear a 1-carbethoxy-1-cyanomethyl substituent in the pyridine ring. Part 2" JOURNAL OF HETEROCYCLIC CHEMISTRY (1987), 24(5), 1467-72 , XP009011734 page 1468; example 9	9
X	KLEMM, L. H. ET AL: "Chemistry of thienopyridines. XXXII. Direct introduction of C-substituents gamma to the heteronitrogen atom in the thieno'2,3-b!pyridine system" JOURNAL OF HETEROCYCLIC CHEMISTRY (1984), 21(4), 1135-40 , XP009011735 Tautomeric forms A and B page 1136	9
A	EP 0 780 119 A (GIVAUDAN ROURE INT) 25 June 1997 (1997-06-25) cited in the application the whole document	1
A	US 5 605 680 A (COTTERET JEAN ET AL) 25 February 1997 (1997-02-25) cited in the application the whole document	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/01049

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 9,10 (both partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 9,10 (both partially)

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claim(s) is impossible. Consequently, the search has been restricted to:

the compounds claimed according to claim 9 wherein R1 and R2 have been limited to the meanings given on page 1, last paragraph of the description.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/01049

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
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(75) Inventor/Applicant *(for US only)*: **BERG-SCHULTZ, Katja** [DE/CH]; Auf der Schanz 51, CH-4303 Kaiseraugst (CH).

(74) Agents: **DR. LEDERER, Franz** et al.; Prinzregentenstrasse 16, 80538 München (DE).

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Published:
— *with international search report*

(88) Date of publication of the revised international search report: 6 November 2003

(15) Information about Correction:
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SUNSCREEN COMPOSITIONS AS WELL AS DIHYDROPYRIDINES AND DIHYDROPYRANES

(57) Abstract: 1,4-dihydropyridine and 1,4-dihydropyrane derivatives and novel cosmetic or dermatological sunscreen compositions containing novel and/or known 1,4- dihydropyridine or 1,4-dihydropyrane derivatives which are useful for photoprotecting human skin and/or hair against UV radiation, in particular solar radiation, and the use of such 1,4-dihydropyridine and/or 1,4-dihydropyrane derivatives as UV-A screening agents, particularly in cosmetic and pharmaceutical compositions.

WO 03/068183 A1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/01049

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KLEMM, L. H. ET AL: "Chemistry of thienopyridines. XLII. Three novel compounds derived from thienopyridine N-oxides [1]" JOURNAL OF HETEROCYCLIC CHEMISTRY (1994), 31(1), 161-3 , XP009011732 Compound a (tautomerism 7) Compound a (tautomerism 9) --- -/--	9

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 August 2003	21. 08. 2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Goss, I

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/01049

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KLEMM, L. H. ET AL: "Chemistry of thienopyridines. XXXV. Synthesis, tautomerism, and reactions of quinoline and thienopyridine systems which bear a 1-carbethoxy-1-cyanomethyl substituent in the pyridine ring. Part 2" JOURNAL OF HETEROCYCLIC CHEMISTRY (1987), 24(5), 1467-72 , XP009011734 page 1468; example 9 ---	9
X	KLEMM, L. H. ET AL: "Chemistry of thienopyridines. XXXII. Direct introduction of C-substituents gamma to the heteronitrogen atom in the thieno[2,3-b]pyridine system" JOURNAL OF HETEROCYCLIC CHEMISTRY (1984), 21(4), 1135-40 , XP009011735 Tautomeric forms A and B . page 1136 ---	9
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A	US 5 605 680 A (COTTERET JEAN ET AL) 25 February 1997 (1997-02-25) cited in the application the whole document -----	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/01049

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 9,10 (both partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 9,10 (both partially)

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claim(s) is impossible. Consequently, the search has been restricted to:

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